



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09K 7/02	A1	(11) International Publication Number: WO 99/48994 (43) International Publication Date: 30 September 1999 (30.09.99)
(21) International Application Number: PCT/SE99/00253 (22) International Filing Date: 24 February 1999 (24.02.99) (30) Priority Data: 9800958-2 23 March 1998 (23.03.98) SE (71) Applicant (for all designated States except US): PERSTORP AB [SE/SE]; S-284 80 Perstorp (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): SJÖGREEN, Carl-Axel [SE/SE]; Spjutserödsvägen 44, S-284 37 Perstorp (SE). SALLMÉN, Bengt [SE/SE]; Bovetevägen 16, S-260 40 Viken (SE). (74) Agent: STENBERG, Yngve; Perstorp AB, S-284 80 Perstorp (SE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A MIXED FORMATE AND BROMIDE BRINE USED IN DRILLING FLUIDS (57) Abstract <p>The use of a saturated aqueous salt solution, comprising at least one formate salt and at least one bromide salt, in a drilling fluid. Said saturated aqueous salt solution comprises 40–50 % by weight of water and 50–60 % by weight of said salts in a weight ratio formate to bromide of 30:70 to 60:40. Preferred salts are alkali metal formates and bromides. The saturated aqueous salts solution has a density and a total salt content exceeding that of a saturated aqueous solution of said bromide salt.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

A MIXED FORMATE AND BROMIDE BRINE USED IN DRILLING FLUIDS

The present invention relates to the use of a saturated aqueous solution, comprising at least one formate salt and at least one bromide salt, in drilling fluids

Well servicing fluids, such as drilling fluids, for land based as well as offshore oil drilling have normally and for many years been oil based. Changes in the environmental legislation have forced the industry to seek other types of drilling fluids and a frequently applied solution is the use of a pseudo oil based mud, which is based on synthetic hydrocarbons. However, these systems are still not proven to be environmentally fully acceptable and their future is uncertain. The main concern is biodegradation, both aerobic and anaerobic. Common to all is that they do affect the environment, either by staying on the seabed for many years or by degrading rapidly with short but more drastic effects on the environment.

However, not only environmental requirements have to be considered when selecting a drilling fluid. Also technical requirements have to be fulfilled, such as high solubility, high density, good temperature stability, good hydrolytic properties, shale stability, tolerance to contamination, material compatibility, reservoir compatibility and recycling possibilities. Conventional water based drilling fluids can often not compete with the oil based or pseudo oil based systems in most of these areas. Drilling fluids based on brines, such as formates or bromides, however, have been found to fulfil all of the above mentioned requirements. Bromides give in general higher water solubility and higher densities than formates, but are however more expensive and less environmentally safe.

Low solids drilling fluids based on formates were originally designed to minimise frictional pressure losses in slim hole drilling. In addition, their unique capability of stabilising polymers to high temperatures made them more temperature resistant than any other polymer based drilling fluids. Formates and bromides are, because of their high density and low corrosivity, ideal completion and packer fluids and are compatible with reservoir fluids, good shale stabilisers, gas hydrate inhibitors and scale dissolvers. Formates have for instance also been shown to be environmentally more acceptable than other commonly used brine system, shale stabilising and compatible with reservoir fluids and common drilling equipment materials. At higher densities, however, the formates are the only known brines that can increase the transition temperature of xanthan.

It has from the present invention quite unexpectedly been found that mixed brines comprising at least one formate salt and at least one bromide salt advantageously can be used in drilling fluids, such as oil well drilling fluids. The total solubility, that is the total salt content and the

density of the brine, at a given temperature is for the mixed brine according to the present invention higher than the solubility for respective salt.

The brine use according to the present invention is a saturated aqueous solution comprising 40-50% by weight of water and 50-60% by weight of salts. The salts are at least one formate, preferably an alkali metal formate, and at least one bromide, likewise preferably an alkali metal bromide in a weight ratio formate to bromide of 30:70 to 60:40. Said saturated aqueous solution has a higher salt content and a higher density than can be obtained with respective included salt per se and most important higher than a saturated aqueous solution of included bromide salt.

The salts of the aqueous solution used according to the present invention are as previously disclosed preferably salts of alkali metals and may thus include formates and bromides of the same or different alkali metals or combinations of different alkali metal formates and/or bromides. The preferred alkali metals include potassium, sodium and/or caesium. The most preferred alkali metal is sodium.

Saturated aqueous solutions of sodium formate and sodium bromide are suitably prepared at a temperature of 0-50°C giving a brine density of for instance 1.50-1.60 g/cm³. A preferred temperature range is 5-15°C, such as 8-12°C, whereby the density of the brine at said temperature is 1.51-1.54 g/cm³. A further suitable preparation temperature is to be found within the range of 15-30°C, such as 20-25°C, whereby the density of the brine at said temperature is 1.53-1.57 g/cm³.

Advantages obtained by using the saturated aqueous salt solution of the present invention in comparison to the use of bromide salts can be summarised:

- a higher density than for included bromide salt per se,
- higher total salt than obtained with included bromide per se,
- formates has a stabilising effect on for instance thickening agents,
- formates increases the high temperature stability,
- formates are less expensive than bromides.

These and other objects and the attendant advantages will be more fully understood from the following detailed description, taken in conjunction with Examples 1 and, wherein Example 1 discloses preparation at 22°C of saturated aqueous salts solutions comprising sodium formate and sodium bromide and Example 2 is Example 1 repeated at a temperature of 10°C. While particular embodiments of the invention is shown, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore,

contemplated to cover by the appended Claims any such modifications as fall within the true spirit and scope of the invention.

Example 1

Five (5) saturated aqueous solutions, four (A-D) being inside the scope of the invention and one (E) being outside said scope, comprising sodium formate and sodium bromide were prepared by mixing in 40% by weight of water:

- A) 15% by weight of sodium formate and 45% by weight of sodium bromide,
- B) 25% by weight of sodium formate and 35% by weight of sodium bromide,
- C) 30% by weight of sodium formate and 30% by weight of sodium bromide,
- D) 35% by weight of sodium formate and 25% by weight of sodium bromide,
- E) 45% by weight of sodium formate and 15% by weight of sodium bromide,

The mixtures were under stirring allowed to obtain a solution equilibrium at 22°C. Undissolved salts were now removed by filtering in a tempered (22°C) filter and analysed:

Solution no.	Sodium Formate Content, %-w/w	Sodium Bromide Content, %-w/w	Total Salt Content %-w/w	Density g/cm ³
A	17.7	36.8	54.5	1.545
B	26.2	31.9	58.1	1.565
C	26.0	30.4	56.4	1.561
D	29.0	27.9	56.0	1.532
E	36.2	17.4	53.6	1.457

Following values are valid for respective salt at 22°C:

Salt	Solubility in Water %-w/w	Saturated Aqueous Solution Density g/cm ³
Sodium formate	45 ^{*1}	1.318 ^{*2}
Sodium bromide	47.8 ^{*2}	1.520 ^{*2}

*1 According to Groschuff, Ber. 36, 1788 (1903)

*2 According to Perstorp Polyols, 1997

Example 2

Five (5) saturated aqueous solutions, four (A-D) being inside the scope of the invention and one (E) being outside said scope, comprising sodium formate and sodium bromide were prepared by mixing in 40% by weight of water:

- A) 15% by weight of sodium formate and 45% by weight of sodium bromide,
- B) 25% by weight of sodium formate and 35% by weight of sodium bromide,
- C) 30% by weight of sodium formate and 30% by weight of sodium bromide,
- D) 35% by weight of sodium formate and 25% by weight of sodium bromide,
- E) 45% by weight of sodium formate and 15% by weight of sodium bromide,

The mixtures were under stirring allowed to obtain a solution equilibrium at 10°C. Undissolved salts were now removed by filtering in a tempered (10°C) filter and analysed:

Solution no.	Sodium Formate Content, %-w/w	Sodium Bromide Content, %-w/w	Total Salt Content %-w/w	Density g/cm ³
A	19.1	33.4	52.5	1.526
B	28.0	28.0	56.0	1.522
C	28.0	30.3	58.3	1.536
D	28.2	28.6	56.8	1.516
E	35.4	17.8	53.2	1.459

Following values are valid for respective salt at 10°C:

Salt	Solubility in Water %-w/w	Saturated Aqueous Solution Density g/cm ³
Sodium formate	37 ^{*1}	1.258 ^{*2}
Sodium bromide	45.9 ^{*2}	1.493 ^{*2}

*1 According to Groschuff, Ber. 36, 1788 (1903)

*2 According to Perstorp Polyols, 1997

As can be seen from solutions A-D of Examples 1 and 2, the total solubility (total salt content) at respective temperature is higher than the solubility for respective salt. It can from solutions A-D of Examples 1 and 2, furthermore, be seen that the density of the mixed solutions are higher than the density for sodium bromide as well as for sodium formate at respective temperature.

CLAIMS

1. Use of a saturated aqueous salt solution in a drilling fluid, said salt solution comprising at least one formate salt and at least one bromide salt,
characterised in,
that said saturated aqueous salt solution comprises 40-50% by weight of water and 50-60% by weight of said salts in a weight ratio formate to bromide of 30:70 to 60:40, said saturated aqueous salt solution having a density and a total salt content exceeding that of a saturated aqueous solution of said bromide salt.
2. Use according to Claim 1
characterised in,
that said salts independently are salts of at least one alkali metal.
3. Use according to Claim 2
characterised in,
that said alkali metal is potassium, sodium or caesium or a combination thereof.
4. Use according to any of the Claims 1-3
characterised in,
that said formate salt is sodium formate and said bromide salt is sodium bromide.
5. Use according to Claim 4
characterised in,
that said saturated aqueous solution is prepared at a temperature of 5-15°C, preferably 8-12°C, and has a density of 1.51-1.54 g/cm³ at said temperature.
6. Use according to Claim 4
characterised in,
that said aqueous solution is prepared at a temperature of 15-30°C, preferably 20-25°C, and has a density of at least 1.53-1.57 g/cm³ at said temperature.
7. Use according to any of the Claims 1-6
characterised in,
that said drilling fluid is an oil well drilling fluid.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/00253

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2250761 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 17 June 1992 (17.06.92), page 4, line 23 - page 5, line 7 --	1-7
A	WO 9726311 A1 (GREAT LAKES CHEMICAL CORPORATION), 24 July 1997 (24.07.97), specially example 1, page 26, line 16 --	1-7
A	US 5728652 A (JAMES W. DOBSON, JR. ET AL), 17 March 1998 (17.03.98), specially claim 1 -- -----	1-7

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 June 1999

Date of mailing of the international search report

23 -06- 1999

Name and mailing address of the ISA/

Swedish Patent Office

Authorized officer

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/06/99

International application No.

PCT/SE 99/00253

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
GB	2250761	A	17/06/92	NONE	
WO	9726311	A1	24/07/97	EP 0874878 A NO 983242 A	04/11/98 15/09/98
US	5728652	A	17/03/98	AU 701372 B AU 5594696 A CA 2178767 A EP 0786507 A NO 963296 A US 5728654 A AU 699954 B AU 4214896 A CA 2167003 A EP 0726302 A NO 960500 A US 5616541 A US 5641728 A	28/01/99 27/02/97 26/02/97 30/07/97 10/02/97 17/03/98 17/12/98 22/08/96 11/08/96 14/08/96 12/08/96 01/04/97 24/06/97